(12) **EUROPEAN PATENT APPLICATION**

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(54) **Method of manufacturing high-temperature shape memory alloys**

(57) The method comprises the steps of cold-working a high - temperature shape memory alloy, in which a reverse martensite transformation start temperature (As) in the first heating after cold working reaches 350°C or above, thereafter heating the cold-worked alloy as a first heat treatment for a period of incubation time or less of recrystallization at a temperature higher than a reverse martensite transformation finish temperature (Af) in the first heating after cold working, and finally annealing the resultant alloy as a second heat treatment at a temperature which is not less than a plastic strain recovery temperature and not more than a recrystallization temperature. Specifically, the first heat treatment is performed for a period of three minutes or less at a temperature which exceeds 500°C and is less than a melting point of the alloy. The composition of the high-temperature shape memory alloy is expressed as $Ti_{50}Ni_{50-x}Pd_x$ (x being set in the range of 35 to 50 at %), $Ti_{50-x}Ni_{50}Zr_x$ (x being set in the range of 22 to 30 at %), $Ti_{50-x}Ni_{50}Hf_x$ (x being set in the range of 20 to 30 at %) or the like.

Description

This invention relates to a method of manufacturing high-temperature shape memory alloys, and more particularly, to a manufacturing method for substantially improving shape recovery characteristics of high-temperature shape memory alloys such as Ti-Pd-Ni, Ti-Ni-Zr and Ti-Ni-Hf alloys.

Description of the Prior Art:

Ti-Ni alloys are well known as shape memory alloys and superelastic alloys. A shape recovery temperature (i.e., reverse martensite transformation finish temperature, which will hereafter be referred to as Af temperature) can be varied in the range of approximately -100 to +100°C depending on a composition ratio of Ti to Ni, addition of a third element and conditions of thermo-mechanical treatment or the like.

In case of shape memory treatment, these shape memory alloys are cold-worked and thereafter annealed at a temperature (approximately 400°C in general) which is not less than a plastic strain recovery temperature. The plastic strain recovery temperature corresponds to a temperature, at which dislocations induced by cold working are rearranged. Since the plastic strain recovery temperature is higher than the Af temperature, the shape memory alloys are heated up to the Af temperature or above simultaneously with annealing for the shape memory treatment and then transformed to a parent phase state once to permit the memory of shape.

It is important for the shape memory treatment to satisfy the following three conditions for obtaining satisfactory shape memory characteristics. 1) Saturation of reorientation of martensite variants due to cold working should be settled. 2) Dislocations induced by cold working should be rearranged. 3) No recrystallization should be caused.

The Af temperature (shape recovery temperature) of Ti-Ni shape memory alloys slightly exceeds 100°C at most. Thus, in order to obtain shape memory alloys requiring Af temperature higher than 100°C, i.e., high-temperature shape memory alloys, it is necessary to substitute different kinds of alloys such as Ti-Ni-Pd and Ti-Ni-Zr alloys for Ti-Ni alloys.

The high-temperature shape memory alloys can be used for components operated by detecting the boil of water, the overheat of oil and the melting of polymer or the like, or safety valves for cooling water in nuclear reactors.

A large number of alloys such as Ti-Pd-X, Ti-Au-X (X=Ni, Cu, W, Ta, Co, Cr, Fe) and Ti-Ni-X (X=Zr, Hf) alloys are well known as the high-temperature shape memory alloys, in which the Af temperature largely exceeds 100°C. These alloys can vary a reverse martensite transformation start temperature (hereafter will be referred to as As temperature) or the Af temperature depending on the kind of substituent element and the composition range thereof. The As or Af temperature may reach 500°C or above depending on the composition range.

In general, a difference between the As temperature and the Af temperature in an annealing state is not more than several tens degrees. However, when these alloys are cold-worked, the Af temperature in the first heating after cold working further rises by approximately 150°C due to induction of strain or deformation, and therefore, the difference between the As temperature and the Af temperature widens. Thus, in case of alloys, in which the As temperature is not less than 350°C, the Af temperature in the first heating after cold working reaches 500°C or above to result in exceeding a recrystallization temperature.

For instance, in case where a composition of Ti-Ni-Pd alloy is expressed as $Ti_{50}Ni_{50-x}Pd_x$ (a numerical value represents at %, and the same shall apply hereafter), when x is set to the value of 43 or above, the Af temperature in the annealing state reaches 500°C or above. Further, when x is set to the value of 35 or above, the As temperature is not less than 350°C, and the Af temperature in the first heating after cold working reaches 500°C or above.

In case where a composition of Ti-Ni-Zr alloy is expressed as $Ti_{50-x}Ni_{50}Zr_x$, when x is set to the value of 29 or above, the Af temperature in the annealing state reaches 500°C or above.

When x is set to the value of 22 or above, the As temperature is not less than 350°C, and the Af temperature in the first heating after cold working reaches 500°C or above.

Further, in case where a composition of Ti-Ni-Hf alloy is expressed as $Ti_{50-x}Ni_{50}Hf_x$, when x is set to the value of 27 or above, the Af temperature in the annealing state reaches 500°C or above. Further, when x is set to the value of 20 or above, the As temperature is not less than 350°C, and the Af temperature in the first heating after cold working reaches 500°C or above.

As described above, in case of the alloys, in which the As temperature is not less than 350°C, the Af temperature in the first heating after cold working reaches 500°C or above to result in exceeding a recrystallization temperature. As a matter of course, in case of alloys, in which the As temperature is not less than 500°C from the beginning, the Af temperature in the first heating after cold working is also not less than 500°C.

However, even if such alloys described above are cold-worked and thereafter annealed as heat treatment at 400°C for an hour, similarly to the conventional Ti-Ni shape memory alloys, it is not possible to cause the memory of shape.

On the other hand, when the above alloys are annealed at a temperature higher than the Af temperature in the first heating after cold working, it is possible to cause the memory of shape. However, since the recrystallization starts for the above alloys this time, a shape recovery rate is degraded.

For the reasons described above, the high-temperature shape memory alloys, in which the Af temperature in the first heating after cold working reaches a recrystallization temperature or above, have caused a problem in that a satisfactory shape recovery rate cannot be obtained.

As a result of various examinations about the above problems, the present invention has developed a manufacturing method, in which such a high-temperature shape memory alloy that As temperature in the first heating after cold working is not less than 350°C permits the memory of shape, and a satisfactory shape recovery rate can be attained.

According to the present invention as defined in claim 1 for solving the above problems, there is provided a method of manufacturing a high-temperature shape memory alloy, comprising the steps of cold-working a high-temperature shape memory alloy, in which a reverse martensite transformation start temperature (As) in the first heating after cold working reaches 350°C or above, thereafter heating the cold-worked alloy as a first heat treatment for a period of incubation time or less of recrystallization at a temperature higher than a reverse martensite transformation finish temperature (Af) in the first heating after cold working, and finally annealing the resultant alloy as a second heat treatment at a temperature which is not less than a plastic strain recovery temperature and not more than a recrystallization temperature.

According to the present invention as defined in claim 2, there is provided a method of manufacturing a high-temperature shape memory alloy according to claim 1, wherein the first heat treatment is performed for a period of three minutes or less at a temperature which exceeds 500°C and is less than a melting point of the alloy.

According to the present invention as defined in claim 3, there is provided a method of manufacturing a high-temperature shape memory alloy according to claim 1 or 2, wherein the composition of the high-temperature shape memory alloy is expressed as $Ti_{50}Ni_{50-x}Pd_x$, in which x is set in the range of 35 to 50 at %, $Ti_{50-x}Ni_{50}Zr_x$, in which x is set in the range of 22 to 30 at %, or $Ti_{50-x}Ni_{50}Hf_x$, in which x is set in the range of 20 to 30 at %.

Hereafter will be described the present invention in detail. First of all, a general principle of shape memory treatment of shape memory alloys will be given as follows.

Dislocations are induced at high density in crystal due to cold working. The resultant is annealed for a proper period of time at a proper temperature higher than a plastic strain recovery temperature to cause rearrangement of dislocations. Since the rearranged dislocations offer resistance to slip, the critical stress for the slip is increased more than the critical stress for the rearrangement of martensite or for the appearance of stress-induced martensite. Thus, the martensite or the stress-induced martensite is appeared without causing any slip at the time of deformation to exert satisfactory shape memory characteristics.

On the other hand, when the annealing temperature rises up to the recrystallization temperature or above, not only the dislocations are rearranged, but also the recrystallization is caused. Since a recrystallized portion extremely reduces the density of dislocations, the resistance to the slip is reduced. Therefore, the critical stress for the slip is reduced more than the critical stress for the rearrangement of martensite, and the slip is easily caused to result in degradation of shape memory characteristics.

In case of the conventional Ti-Ni shape memory alloys, since the Af temperature (-100 to 100°C) is not more than the plastic strain recovery temperature (approximately 400°C), the transformation to a parent phase state occurs due to heating up to the plastic strain recovery temperature or above. Accordingly, the rearrangement of dislocations as described above is caused under the condition that the saturation of reorientation of martensite variants caused by cold working is settled. Therefore, the conventional Ti-Ni shape memory alloys permit the memory of shape, and has no problem.

However, in case of Ti-Pd-X, Ti-Au-X, Ti-Ni-X or like shape memory alloys, in which the Af temperature is higher than the recrystallization temperature, when the annealing is performed at a temperature exceeding the Af temperature, the recrystallization is caused to degrade the shape recovery characteristics. On the other hand, when the annealing is performed at a temperature less than the Af temperature, the above shape memory alloys remain saturated with respect to reorientation of martensite variants caused by cold working even after the heat treatment, and therefore, the memory of shape cannot be attained.

The present invention has been provided on the basis of the above knowledge. According to the present invention, a high-temperature shape memory alloy, in which As temperature in the first heating after cold working reaches 350°C or above, i.e., Ti-Pd-X, Ti-Au-X, Ti-Ni-X or like alloy described above is cold-worked and thereafter heated as the first heat treatment for a period of incubation time or less of recrystallization at a temperature higher than the Af temperature in the first heating after cold working.

The crystal structure of the alloy is transformed to the parent phase by the first heat treatment.

Once the crystal structure of the alloy is transformed to the parent phase, the saturation of reorientation of martensite variants caused by cold working can be settled.

The temperature in the heat treatment described above is set to be not less than the recrystallization temperature of the alloy. However, since the transformation to the parent phase is finished within the incubation time of recrystallization, the heat treatment for a short period of time is enough for heating to the Af temperature or above, and the start of recrystallization can be avoided.

In other words, the first heat treatment of the present invention is performed at a temperature higher than not only the Af temperature but also the recrystallization temperature. However, since the heating time in the first heat treatment is as extremely short as the incubation time or less of recrystallization, the shape memory alloy having a high shape recovery rate can be obtained without causing recrystallization.

The temperature in the first heat treatment preferably exceeds 500°C and is less than a melting point of the alloy. When the temperature is less than 500°C, the shape recovery rate is degraded. On the other hand, when the temperature exceeds the melting point, the alloy is melted. The temperature in the range of 500 to 1000°C is preferably of practical use.

For instance, the melting point of Ti-Au-Ni alloy is approximately in the range of 1310 to 1495°C, the melting point of Ti-Ni-Pd alloy is approximately in the range of 1310 to 1400°C, the melting point of Ti-Ni-Zr alloy is approximately in the range of 1260 to 1310°C, and the melting point of Ti-Ni-Hf alloy is approximately in the range of 1310 to 1530°C.

The recrystallization temperature of each of the above alloys is not less than 500°C.

The heating time in the first heat treatment is preferably set to be within three minutes. When the heating time exceeds three minutes, the recrystallization is caused to degrade the shape recovery characteristics. More preferably, the heating time is set to be within one minute.

After the first heat treatment, the annealing is performed as the second heat treatment at a temperature which is not less than the plastic strain recovery temperature of the alloy and not more than the recrystallization temperature. The second heat treatment causes only the rearrangement of dislocations without recrystallization. Therefore, the satisfactory shape memory effects can be obtained by the second heat treatment.

The second heat treatment is preferably performed at a temperature of 300 to 500°C for 30 minutes to 2 hours. When the temperature is less than 300°C, it is not possible to satisfactorily cause the memory of shape. On the other hand, when the temperature is not less than 500°C, it is liable to cause the recrystallization.

The high-temperature shape memory alloy to be manufactured according to the present invention corresponds to an alloy, in which the As temperature in the first heating after cold working reaches 350°C or above, i.e., a shape memory alloy recovering at a temperature as high as 350°C or above. At present, the Ti-Pd-X, Ti-Au-X (X=Ni, Cu, W, Ta, Co, Cr, Fe), and Ti-Ni-X (X=Zr, Hf) alloys described above are noticeable as the high-temperature shape memory alloys. In particular, the Ti-Pd-X and Ti-Ni-X alloys are of practical use. From the viewpoint of a composition, a alloys having the compositions respectively expressed as $Ti_{50}Ni_{50-x}Pd_x$, in which x is in the range of 35 to 50 at %, $Ti_{50-x}Ni_{50}Zr_x$, in which x is in the range of 22 to 30 at %, and $Ti_{50}Ni_{50}Hf_x$, in which x is in the range of 20 to 30 at %, show satisfactory characteristics and are preferably of practical use.

These high-temperature shape memory alloys can be manufactured according to an ordinary method. For instance, a billet is manufactured by means of high frequency induction melting, plasma melting, powder metallurgy or the like. Subsequently, the billet thus manufactured is hot-worked by means of hot rolling, hot extrusion or the like, and then cold-worked by means of cold rolling, drawing or the like to be worked into a sheet, strip, rod, wire or like material.

An ordinary heating furnace may be used in the heat treatment. High frequency heating, annealing by direct current or the like can be applied to the heat treatment. Also, air cooling, water quenching or the like can be properly used for cooling after annealing.

Hereafter will be described a preferred embodiment of the present invention by contrast with comparative examples.

(Embodiment 1)

An alloy having a composition expressed as $Ti_{50}Ni_{50-x}Pd_x$ was used to prepare three kinds of samples varying in concentration of Pd such that x is set to 35, 40 and 50 at %, respectively. 30g of each sample was melted by means of plasma melting and worked into a sheet of 1.0 mm in thickness through hot rolling and cold rolling (cold-rolling work rate: approximately 25 %). A tension test piece (of 16 mm in gauge length) was cut off from the sheet by means of electric discharge machining. The surface of each test piece was polished, and thereafter, each test piece was heat-treated at various temperatures shown in Table 1.

A test for shape recovery characteristics was given to each test piece. The results are shown in Table 1.

With respect to test pieces remaining approximately 3 % of apparent plastic strain resulting from the removal of stress after 4 % of tensile strain has been applied to the test pieces at room temperature, the evaluation was made as follows. When the above test pieces were heated up to the shape recovery test temperature shown in Table 1 to cause reverse transformation, the test pieces having shown an almost 100 % shape recovery rate were represented by O (i. e., the shape recovery rate was not less than 95 %), the test pieces having hardly shown recovery of shape were represented by X (i.e., the shape recovery rate was not more than 20 %), and the test pieces intermediate between the test pieces represented by O and X were represented by Δ.

In Table 1, the As temperature in the first heating represents a reverse martensite transformation start temperature in the first heating after cold working. In this case, the As temperature was determined according to a thermal analysis.

In the heat treatment temperatures, Tf represents the temperature in the first heat treatment, and the time to hold the test pieces at Tf was set to one minute, while Ta represents the temperature in the second heat treatment, and the time to hold the test pieces at Ta was set to an hour.

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TABLE 1

NO.	Pd CONCENTRATION x (at%)	REVERSE TRANSFORMATION START TEMPERATURE IN FIRST HEATING As (°C)	HEAT TREATMENT TEMPERATURE		SHAPE RECOVERY CHARACTERISTICS		REMARKS
			Tf (°C)	Ta (°C)	SHAPE RECOVERY TEST TEMP. (°C)	RECOVERY RATE	
1	35	APPROX. 350	500	400	380	O	PRESENT INVENTION
2	"	"	—	400	"	x	COMPARATIVE EXAMPLE
3	"	"	—	500	"	△	"
4	"	"	—	900	"	△	"
5	"	"	600	400	"	O	PRESENT INVENTION
6	40	APPROX. 520	570	400	460	O	PRESENT INVENTION
7	"	"	—	400	"	x	COMPARATIVE EXAMPLE
8	"	"	—	900	"	△	"
9	"	"	600	400	"	O	PRESENT INVENTION
10	50	APPROX. 670	730	400	620	O	PRESENT INVENTION
11	"	"	—	400	"	x	COMPARATIVE EXAMPLE
12	"	"	—	900	"	△	"

As is apparent from Table 1, it is found that each of the test pieces Nos. 1, 5, 6, 9 and 10 is not less than 350°C

in As temperature in the first heating after cold working and shows an almost 100% shape recovery rate.

On the other hand, it is found that each of the test pieces Nos. 2, 3, 4, 7, 8, 11 and 12 of the comparative examples hardly shows the recovery of shape, or is inferior in shape recovery rate, since the first heat treatment (Tf) is not performed.

(Embodiment 2)

With respect to the samples of 35 and 40 at % in concentration of Pd according to the embodiment 1, the temperatures (Tf, Ta) and time in the heat treatment were varied as shown in Table 2 to prepare different kinds of samples. The shape recovery characteristics were examined similarly to the embodiment 1, and the results are shown in Table 2.

TABLE 2

NO.	Pd CONCENTRATION x (at %)	HEAT TREATMENT TEMPERATURE		HOLDING TIME (min.)		PRESENCE OF RECRYSTALLIZATION	SHAPE RECOVERY CHARACTERISTICS		REMARKS
		Tf (°C)	Ta (°C)	Tf	Ta		SHAPE RECOVERY TEST TEMP. (°C)	RECOVERY RATE	
1	35	500	400	1	60	ABSENCE	380	O	PRESENT INVENTION
2	"	600	400	2	60	ABSENCE	"	O	"
3	"	600	400	10	60	PRESENCE	"	△	COMPARATIVE EXAMPLE
4	40	570	400	1	60	ABSENCE	460	O	PRESENT INVENTION
5	"	600	400	30(sec.)	60	ABSENCE	"	O	"
6	"	600	400	10	60	PRESENCE	"	△	COMPARATIVE EXAMPLE

As is apparent from Table 2, each of the test pieces Nos. 1, 2, 4 and 5 of the present invention shows satisfactory

shape recovery characteristics without causing recrystallization. In this case, as long as the time to hold the test pieces at Tf is within 2 minutes, the first heat treatment can be performed within the incubation time of recrystallization, even if Tf exceeds the recrystallization temperature.

On the other hand, each of the test pieces Nos. 3 and 6 of the comparative examples causes recrystallization and is inferior in shape recovery characteristics, since the test pieces are held at Tf for a long period of time.

(Embodiment 3)

An alloy having a composition expressed as $Ti_{50-x}Ni_{50}Zr_x$ was used to prepare two kinds of samples varying in concentration of Zr such that x is set to 22 and 30 at %, respectively. 3Kg of each sample was melted by means of high frequency induction melting, and then subjected to casting, hot-extrusion and hot-rolling with a grooved roll. Subsequently, the resultant was repeatedly drawn with a dies and annealed to be worked into a wire of 1.0 mm in diameter (final cold working rate: approximately 30 %). 140 mm of the rod was cut off, then linearly fixed in position and heat-treated at various temperatures shown in Table 3.

A test for shape recovery characteristics was given to each test piece. The results are shown in Table 3.

A strain gauge of 50 mm in length between gauges was used for applying tensile strain. The evaluation method, the heat-treatment method and the symbols in Table 3 are similar to those in embodiment 1.

TABLE 3

NO.	Zr CONCENTRATION x (at%)	REVERSE TRANSFORMATION START TEMPERATURE IN FIRST HEATING As (°C)	HEAT TREATMENT TEMPERATURE		SHAPE RECOVERY CHARACTERISTICS		REMARKS
			T_1 (°C)	T_a (°C)	SHAPE RECOVERY TEST TEMP. (°C)	RECOVERY RATE	
1	22	APPROX. 350	600	450	380	O	PRESENT INVENTION
2	"	"	—	400	"	×	COMPARATIVE EXAMPLE
3	"	"	—	600	"	△	"
4	30	APPROX. 500	700	400	530	O	PRESENT INVENTION
5	"	"	—	400	"	×	COMPARATIVE EXAMPLE
6	"	"	—	700	"	△	"

As is apparent from Table 3, each of the test pieces Nos. 1 and 4 of the present invention is not less than 350°C

in As temperature in the first heating, and shows almost 100% shape recovery characteristics. On the other hand, each of the test pieces Nos. 2, 3, 5 and 6 of the comparative examples hardly shows the recovery of shape or is inferior in shape recovery rate, since the first heat treatment (Tf) is not performed.

(Embodiment 4)

With respect to the samples of 22 and 30 at % in concentration of Zr according to the embodiment 3, the temperatures (Tf, Ta) and time in the heat treatment were varied as shown in Table 4 to prepare different kinds of samples. Then, the shape recovery characteristics were examined similarly to the embodiment 3. The results are shown in Table 4.

TABLE 4

NO.	Zr CONCENTRATION x (at %)	HEAT TREATMENT TEMPERATURE		HOLDING TIME (min.)		PRESENCE OF RECRYSTALLIZATION	SHAPE RECOVERY CHARACTERISTICS		REMARKS
		Tf (°C)	Ta (°C)	Tf	Ta		SHAPE RECOVERY TEST TEMP. (°C)	RECOVERY RATE	
1	22	600	400	—	60	ABSENCE	380	O	PRESENT INVENTION
2	"	600	400	10	60	PRESENCE	"	△	COMPARATIVE EXAMPLE
3	30	700	400	—	60	ABSENCE	530	O	PRESENT INVENTION
4	"	700	400	10	60	PRESENCE	"	△	COMPARATIVE EXAMPLE

As is apparent from Table 4, each of the test pieces Nos. 1 and 3 of the present invention shows satisfactory shape

recovery characteristics without causing recrystallization. In this case, as long as the time to hold the test pieces at Af is within one minute, the first heat treatment can be performed with the incubation time of recrystallization, even if Tf exceeds the recrystallization temperature.

On the other hand, each of the test pieces Nos. 2 and 4 of the comparative examples causes recrystallization and is inferior in shape recovery characteristics, since the test pieces are held at Tf for a long period of time.

(Embodiment 5)

An alloy having a composition expressed as Ti_{50-x} $Ni_{50}Hf_x$ was used to prepare two kinds of samples varying in concentration of Hf such that x is set to 20 and 30 at %, respectively. 1Kg of each sample was formed into a billet by means of powder metallurgy. Subsequently, the billet was subjected to hot isostatic press treatment, hot-extrusion and hot-rolling with a grooved roll. Thereafter, the resultant was repeatedly drawn with a dies and annealed to be worked into a wire of 1.0 mm in diameter (final cold working rate: approximately 30 %). 140 mm of the rod was cut off, then linearly fixed in position and heat-treated at various temperatures shown in Table 5. A test for shape recovery characteristics was given to each test piece. The results are shown in Table 5.

The testing method, the evaluation method, the heat-treatment method and the symbols in Table 5 are similar to those in the embodiment 3.

TABLE 5

NO.	Hf CONCENTRATION x (at%)	REVERSE TRANSFORMATION START TEMPERATURE IN FIRST HEATING As (°C)	HEAT TREATMENT TEMPERATURE		SHAPE RECOVERY CHARACTERISTICS		REMARKS
			Tf (°C)	Ta (°C)	SHAPE RECOVERY TEST TEMP. (°C)	RECOVERY RATE	
1	20	APPROX. 350	600	400	390	O	PRESENT INVENTION
2	"	"	—	400	"	×	COMPARATIVE EXAMPLE
3	"	"	—	600	"	△	"
4	30	APPROX. 600	800	400	640	O	PRESENT INVENTION
5	"	"	—	400	"	×	COMPARATIVE EXAMPLE
6	"	"	—	800	"	△	"

As is apparent from Table 5, each of the test pieces Nos. 1 and 4 of the present invention is not less than 350°C

in As temperature in the first heating, and shows an almost 100 % shape recovery rate. On the other hand, each of the test pieces Nos. 2, 3, 5 and 6 of the comparative examples hardly shows the recovery of shape or is inferior in shape recovery rate, since the first heat treatment (Tf) is not performed.

5 (Embodiment 6)

With respect to the samples of 20 and 30 at % in concentration of Hf according to the embodiment 5, the temperatures (Tf, Ta) and time in the heat treatment were varied as shown in Table 6 to prepare different kinds of samples. Then, the shape recovery characteristics were examined similarly to the embodiment 5. The results are shown in Table 10 6.

TABLE 6

NO.	Hf CONCENTRATION x (at%)	HEAT TREATMENT TEMPERATURE		HOLDING TIME (min.)		PRESENCE OF RECRYSTALLIZATION	SHAPE RECOVERY CHARACTERISTICS		REMARKS
		Tf (°C)	Ta (°C)	Tf	Ta		SHAPE RECOVERY TEST TEMP. (°C)	RECOVERY RATE	
1	20	600	400	—	60	ABSENCE	390	O	PRESENT INVENTION
2	"	600	400	10	60	PRESENCE	"	Δ	COMPARATIVE EXAMPLE
3	30	800	400	—	60	ABSENCE	640	O	PRESENT INVENTION
4	"	800	400	10	60	PRESENCE	"	Δ	COMPARATIVE EXAMPLE

As is apparent from Table 6, each of the test pieces Nos. 1 and 3 of the present invention shows satisfactory shape

recovery characteristics without causing recrystallization. In this case, as long as the time to hold the test pieces at Tf is within one minute, the first heat treatment can be performed within the incubation time of recrystallization, even if Tf exceeds the recrystallization temperature.

On the other hand, each of the test pieces Nos. 2 and 4 of the comparative examples causes recrystallization and is inferior in shape recovery characteristics, since the test pieces are held at Tf for a long period of time.

According to the present invention, it is possible to obtain a high-temperature shape memory alloy which is excellent in shape recovery characteristics. Thus, the high-temperature shape memory alloy of the present invention can be expected to be used for components operated by detecting the boil of water, the overheat of oil, and the melting of polymer or the like, or safety valves for cooling water in nuclear reactors.

Claims

1. A method of manufacturing a high-temperature shape memory alloy, characterized by the steps of :

    cold-working a high-temperature shape memory alloy, in which a reverse martensite transformation start temperature (As) in the first heating after cold working reaches 350°C or above;
    thereafter heating the cold-worked alloy as a first heat treatment for a period of incubation time or less of recrystallization at a temperature higher than a reverse martensite transformation finish temperature (Af) in the first heating after cold working; and
    finally annealing the resultant alloy as a second heat treatment at a temperature which is not less than a plastic strain recovery temperature and not more than a recrystallization temperature.

2. A method of manufacturing a high-temperature shape memory alloy according to claim 1, characterized in that the first heat treatment is performed for a period of three minutes or less at a temperature which exceeds 500°C and is less than a melting point of the alloy.

3. A method of manufacturing a high-temperature shape memory alloy according to claim 1 or 2, characterized in that the composition of said high-temperature shape memory alloy is expressed as $Ti_{50}Ni_{50-x}Pd_x$ (a numerical value represents at % and the same shall apply hereafter), in which X is set in the range of 35 to 50 at %, $Ti_{50-x}Ni_{50}Zr_x$, in which X is set in the range of 22 to 30 at %, or $Ti_{50-x}Ni_{50}Hf_x$, in which X is set in the range of 20 to 30 at %.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 January 1996	Gregg, N

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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